

Construction and characterization of solid-state ion flux controller

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An ion flux control device is a key component for interfacing between an artificial electrical system and a cellular-, or bio-system. We prepared a solid-state ion flux control device by combination between polyacrylonitrile (PAN)-based solid polymer electrolyte and cation-dope type polyaniline (c-PANI) which consists of polyaniline and poly(*p*-styrenesulfonic acid)-based dopant. The prototype device had an H-shaped PAN-based film on an insulator plate. The central part (the horizontal bar of the H-shaped film) of the PAN-based electrolyte film was sandwiched between the c-PANI electrode as an ion-storage and release film and the Pt plate as a counter electrode. We confirmed ion flux control of the device by AC impedance measurement of the PAN-based electrolyte film. When the c-PANI film was oxidized electrochemically, the conductivity of the PAN-based electrolyte film decreased. This suggests that the c-PANI film is doped by the oxidation process, lithium ions in the PAN-based electrolyte film are adsorbed from the PAN film to the c-PANI electrode, and the concentration of lithium ions in the PAN-based electrolyte film decreases. When the c-PANI electrode is electrochemically reduced, the lithium ions were released from the c-PANI electrode and conductivity of the PAN-based electrolyte film increases. The conductance agrees with the value recorded before the electrochemical oxidation process of the c-PANI electrode.

Key words: ion flux, solid polymer electrolyte, polyaniline, AC impedance, conductivity

1. INTRODUCTION

Signal transactions and responses in bio-systems are mediated by ion flux, such as calcium, sodium, and potassium ions. For example, the nerve cell shows some impulse consists of two events in order to transfer some information: an influx of positive charge through the membrane due to the movement of sodium ions into the nerve cell, followed by the efflux of positive charge, due to potassium ions. Propagation of the impulse is the basis for communication through the nervous system [1]. Ion flux control on membrane in cell system is performed with ion channels. Ion flux control is a key point process for signal transaction manipulation in cell system.

In our information technology system, a central processing unit (CPU) which is a key part for information process uses flux of electron, *i.e.* current for signal transaction. When we produce a high-performance artificial organ, we need interface system between our artificial electronic device and bio-system (Fig. 1). Total process in an artificial organ is "sensing *in vivo* information", "information processing", and "action to the body". Information processing process will be done by the arithmetic processing by CPU. After the information process the results should transfer from current (electron flux) to ion flux in order to control cellular- or bio-systems. Some devices for interfacing between electric system and bio-system will be required.

In this paper we demonstrated formation of an ion flux control device consisting polyacrylonitrile (PAN)-based electrolyte and cation-dope type polyaniline (c-PANI) electrode. Both materials have

been investigated by our group [2, 3]. As a prototype of ion flux controller, the device which controls the flow of lithium ions was constructed, and its actions and control behavior were examined.

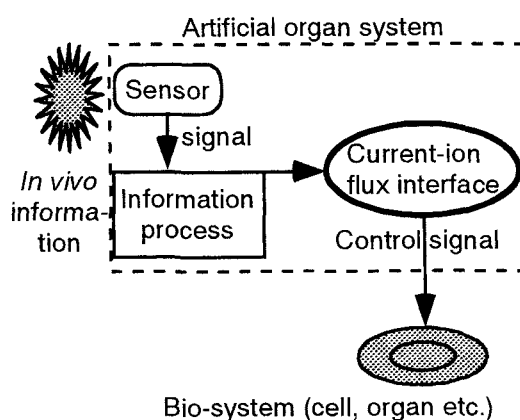


Fig. 1 Schematic presentation of artificial organ system and current-ion flux interface.

2. EXPERIMENTAL

2.1. Materials

All chemicals were purchased and used as received. Polyacrylonitrile (PAN) was purchased from Aldrich Co. and its average molecular weight was 150000.

2.2. Preparation of cation-dope type polyaniline (c-PANI) [2]

Polyaniline (PANI) was prepared by chemical

oxidation of aniline in acidic solution [4].

Polymer dopant, Copolymer(4:6) (Fig. 2), was prepared as follow. Sodium *p*-styrenesulfonate (10.33g, 50 mmol) was dissolved in 200 ml of water. Ion exchange resin (H-type, SK-1B, Mitsubishi Chemical Co.) (2 meq/ml, 50 ml) was added to the solution and shaken for 5 hours. Then the ion exchange resin was removed from the solution by filtration. AM-90G (Shin-Nakamura Chemical Co.) was added to the solution. Loading ratio of AM-90G to *p*-styrenesulfonic acid was 7:3. Polymerization of the mixed solution was initiated by addition of ammonium persulfate and performed under Ar atmosphere at 60°C for 6 hours. Purification of the resulted copolymer was preformed by re-precipitation of the aqueous solution of the polymer into acetone. The composition of the copolymer was determined by NMR measurement. Molar ratio of *p*-styrenesulfonic acid unit to AM-90G unit in the copolymer was 4:6 (Copolymer(4:6)).

Cation-dope type polyaniline (c-PANI) was prepared by mixing polyaniline and Copolymer(4:6) solution. Copolymer(4:6) was dissolved into water and polyaniline was dissolved into *N*-methyl-2-pyrrolidone, respectively. The both solution were mixed each other and stirred for 12 h at room temperature. The resulted particulate was collected by centrifuge process (3000 rpm, 20 min) and the supernatant was removed. The resulted precipitation was preserved in the condition with small amount of NMP.

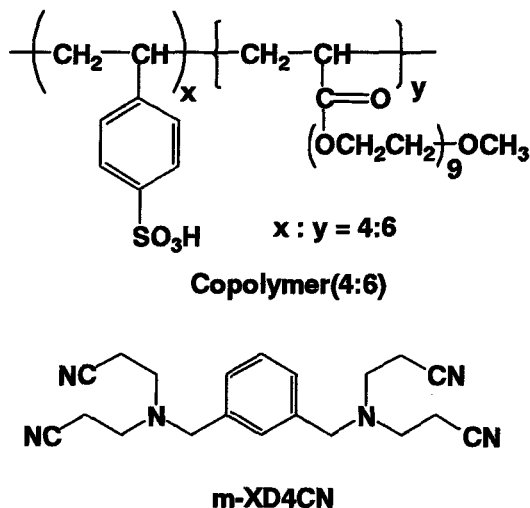


Fig. 2 Structures of Copolymer (4:6) and m-XD4CN.

2.2 Preparation of propylene carbonate solution for polyacrylonitrile(PAN)-based electrolyte film

N, N, N', N'-tetra (2-cyanoethyl)-*m*-xylylenediamine (m-XD4CN) (Fig. 2) was prepared from *m*-xylylenediamine and acrylonitrile [5].

The cast solution for PAN-based electrolyte film consisted of PAN, lithium perchlorate (LiClO_4), m-XD4CN, and propylene carbonate (PC). Typical solution consisted of PAN (0.3024 g), LiClO_4 (0.3026 g), m-XD4CN (0.1926 g), and 10 ml of PC. The mixture was stirred to make the homogeneous PC solution for 12 h at 65°C.

2.3 Construction of solid-state ion flux controller

Fig. 3 shows schematic presentation of a solid-state ion flux controller. The device was constructed on an OHP film (25 mm × 25mm). A Pt plate was installed on the substrate film (Part C in Fig. 3, counter electrode). c-PANI with small amount of NMP was casted on the substrate film (Part D in Fig. 3, control electrode). After removed NMP from the device, the shaped polyethylene film (see Fig. 3(B)). The PC solution (see section 2.2) was poured into the H-shaped hollow. To remove excess PC the device was heated at 70°C for 24 hours under dynamic vacuum condition.

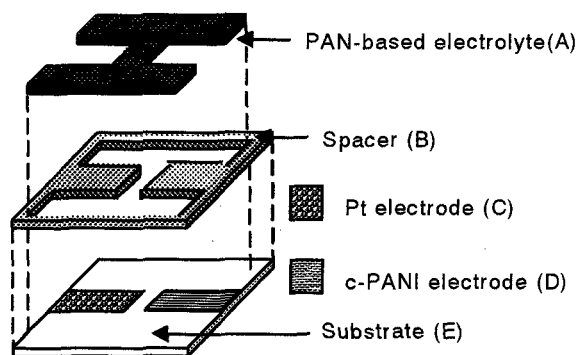


Fig. 3 Schematic presentation of ion flux controller.

2.4 Measurements

Fig. 4 shows the measuring circuit for the evaluation of the ion flux controller. The control and counter electrodes on the device were connected to a potentiostat (HA-301, Hokuto). The conductance measure Pt electrodes were connected to an LCR meter (3522 LCR Hi-tester, Hioki).

Conductivity measurements were performed with the following procedure. Control voltage (V_{cont}) was applied between the c-PANI and Pt electrode (Fig. 3 C and D). The applied voltage as V_{cont} was in the range from 0.1 to 1.0 V. After application of V_{cont} to the device, the potentiostat was detached from the measurement circuit and the impedance between the conductance measure Pt electrodes, immediately. Then the potentiostat was re-attached and other V_{cont} was applied to the device.

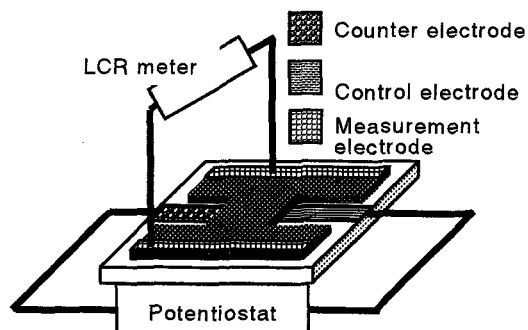


Fig. 4 Schematic presentation of the measuring circuit for the evaluation of the ion flux controller.

3. RESULT AND DISCUSSION

3.1 Effect of applied frequency for AC impedance measurements

Typical AC impedance spectra (Nyquist plots) are shown in Fig. 5. The spectra have no semi-circle in higher frequency region (> 1000 Hz) and the gentle rise curve in lower frequency region (< 1000 Hz). We changed the surface area of the measurement electrodes in order to estimate bulk resistance component of the PAN-based electrolyte and diffused resistor component of the electrolyte.

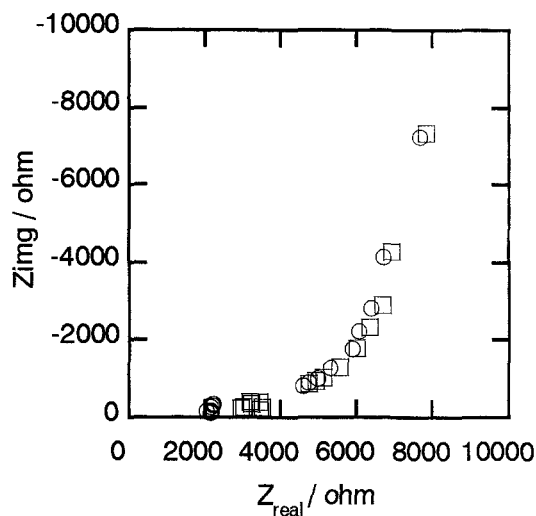


Fig. 5 AC impedance spectra of the control device, $V_{\text{cont}} = 0.6$ V. The contact surface area of the measurement electrode was 2.50 cm^2 (open circle). The contact surface area of the measurement electrode was 1.25 cm^2 (open square).

The resistance value at high frequency region (10 kHz) is $2.1 \text{ k}\Omega$ in the plots of open circle (the measurement electrode area was 2.5 cm^2). The value in the plot of open square is $3.2 \text{ k}\Omega$ (the area was 1.25 cm^2). Relationship between resistance (R) and surface area (A) is presented as following equation (1),

$$R = \frac{1}{\sigma} \times \frac{l}{A} \quad (1)$$

where σ is conductance of the sample and l is the distance between the measurement electrodes. Thus, the resistance value at high frequency region is attributed to bulk resistance of the PAN-based electrolyte. The resistance at lower frequency region is attributed to ion diffusion component in the PAN-based electrolyte.

3.2 Responses of the ion flux controller on applied control voltage (V_{cont})

Fig. 6 shows variation of impedance with applied control voltage (V_{cont}). The impedance values at high frequency (> 1000 Hz) dramatically jumped up with increase of V_{cont} from 0.5 V to 0.6 V. However, the impedance values at lower frequency region (< 1000 Hz) did not change with the change of V_{cont} . As mentioned previous section, the impedance values at lower frequency range are attributed to ion diffusion in

the electrolyte.

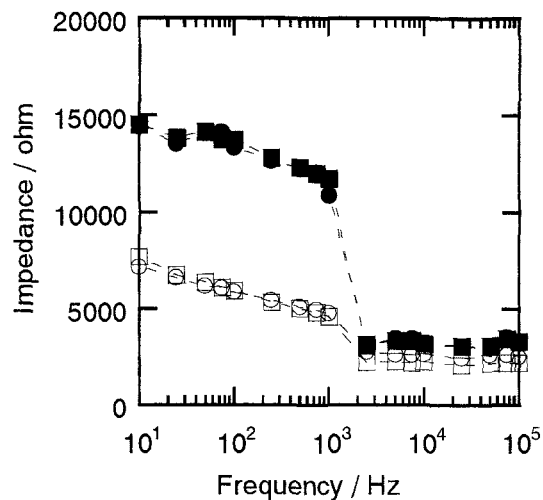


Fig. 6 Variation of impedance for the control device with applied control voltage (V_{cont}). $V_{\text{cont}} = 0.4$ V (open circle), 0.5 V (open square), 0.6 V (solid circle), and 0.7 V (solid square).

We reported that c-PANI is oxidized at 0.7 V vs. SCE in aqueous electrolyte solution [2]. When we applied $V_{\text{cont}} = 0.6$ V to the device, the c-PANI was oxidized and it was doped with lithium ions from the PAN-based electrolyte.

Fig. 7 shows variation of impedance at 1000 Hz with applied control voltage, V_{cont} . The impedance value at 1000 Hz was constant in the range of V_{cont} from 0 V to 0.5 V. Application of $V_{\text{cont}} \geq 0.6$ V induced the increase of the impedance value at 1000 Hz. The impedance value at $V_{\text{cont}} = 0.6$ V is about two-times larger than that at $V_{\text{cont}} = 0.5$ V. The increase of the impedance value suggests that the oxidation reaction of c-PANI by application of $V_{\text{cont}} = 0.6$ V affects the ion flux in the PAN-based electrolyte.

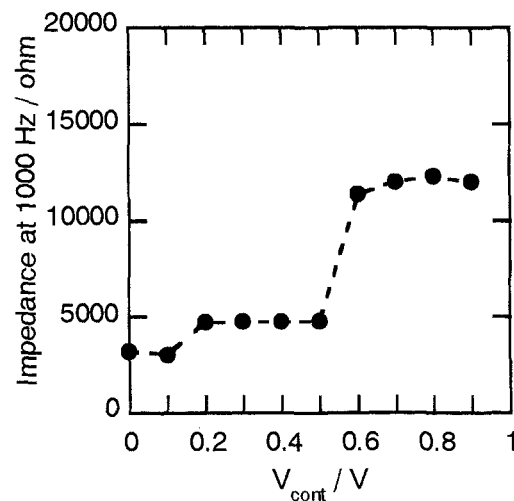


Fig. 7 Variation of impedance at 1000 Hz with applied control voltage (V_{cont}).

Fig. 8 shows the result of examining the reproducibility of the response on applied control voltage (V_{cont}) of the device. The plots at first scan (solid circle) agree with those at second scan (open square). The device had reproducible response.

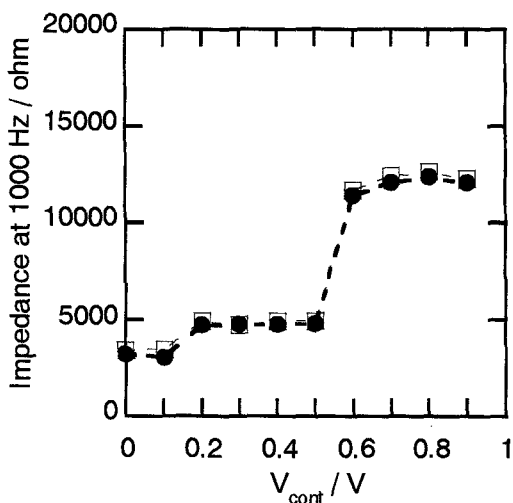


Fig. 8 Variation of impedance at 1000 Hz with applied control voltage (V_{cont}). First scan (solid circle), second scan (open square)

3.3 Operative mechanism of the ion flux control device

We concluded that the mechanism of the impedance change of the device with applied control voltage (V_{cont}) is based on doping and de-doping reaction of c-PANI on the PAN-based electrolyte. Fig. 9 shows the schematic presentation of the mechanism of the ion flux controller. Fig. 9(a) is the oxidation state of the c-PANI electrode. Electrochemical oxidation of the c-PANI electrode induces doping process of lithium ions from the PAN-based electrolyte and the conductivity for the electrolyte decreases. Fig. 9 (b) is the reduction state of the c-PANI electrode. Electrochemical reduction of the c-PANI electrode induces de-doping (release) of lithium ions from the c-PANI electrode and the concentration of lithium ion in the PAN-based electrolyte and the conductivity for the electrolyte increases. Ion concentration in the PAN-based electrolyte is controlled by electrochemical doping and de-doping of the c-PANI electrode and the conductivity of the electrolyte is also changed.

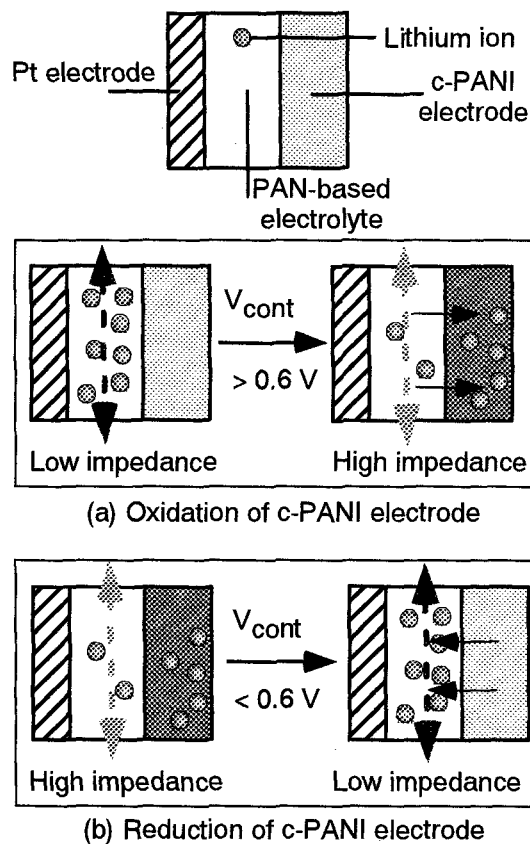


Fig. 9 Schematic presentation of prediction operative mechanism of ion flux controller.

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